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I, KAY WARD, TEAM LEADER EXAMINATION SUPPORT AND SALES hereby certify that annexed is a true copy of the Provisional specification in connection with Application No. PP 5995 for a patent by EMAIL LIMITED filed on 18 September 1998.

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WITNESS my hand this
Twenty-second day of October 1999

K. Ward

KAY WARD
<u>TEAM LEADER EXAMINATION</u>
<u>SUPPORT AND SALES</u>

AUSTRALIA

Patents Act 1990

PROVISIONAL SPECIFICATION

SELF-REGULATING NANOSCALE HEATING ELEMENT

The invention is described in the following statement:

This invention relates to heating elements of the kind including an electrically conductive metal oxide film on an electrically insulating substrate.

Such devices are known, and may for example consists of a thin film of tin oxide deposited on a glass substrate by means of pyrolitic deposition.

If such thin film heating elements are to be used in electrical appliances such as cooktops, it is desirable that they be capable of handling high power densities, of the order of 20 Watts cm^{-2}, and the element must be capable of operating at high temperatures, up to 650°C. Prior art devices have not proved satisfactory in these conditions. Tin oxide layers tend to become unstable with increasing temperature, due to the tendency for the oxide to change state. We have also found that where fluorine is employed as an electron donor or conductivity carrier the properties of the film change irreversibly with increasing temperature, apparently due to the fluorine tending to leave the film at temperatures above 400°C.

We have also found that the tin chloride solutions used in the prior art, for example in the spray pyrolysis process, are not stable in conditions of high humidity, and this can lead to lack of uniformity in the oxide films produced.

US Patent No. 4,889,974 of Auding, *et al.* describes thin film elements intended for temperatures beyond 600°C, using oxide films doped at high levels with pairs of compensating foreign atoms. The metal oxide films are doped with, maximally, 10 mol % of each of the foreign atoms compensating each other in pairs, the quantity of

said acceptor-forming elements and said donor-forming elements differing maximally by 10%. The Auding patent describes the use of indium, boron, aluminium or zinc as the acceptor-forming dopant, and antimony or fluorine as the donor-forming dopant.

However, these films have been found to be difficult to deposit in humid atmospheres and have been found to be unstable in the power densities of approximately 20 Watts per cm^2 required for rapid rise-time applications.

To the applicants' knowledge the films described in the Auding patent have not seen commercial use and are known only from this document.

We have found that a tin oxide layer of satisfactory stability in high power density applications may be obtained by doping with cerium and lanthanum, in quantities up to 5 mol % of each. Preferably these two rare earths are present in substantially equal concentrations.

We have also found that stability at high temperatures may be obtained by further doping with equal quantities of donor and acceptor elements, and by avoiding the use of fluorine as a dopant. The preferred donor and acceptor elements for this purpose are respectively antimony and zinc.

We have also found that superior results can be obtained if the film is prepared by spray pyrolysis from a solution of monobutyl tin trichloride. The stability of this material in high humidity enables consistent results to be obtained across varying atmospheric conditions, by reducing premature oxidation.

The invention provides a thin film heating element which is capable of withstanding power densities of up to 20 Watts cm^{-2} and temperatures in excess of 600°C by depositing thin, electrically-conductive metal oxide films on temperature-stable and relatively chemically inert substrates using organometallic base solutions doped with high quantities of rare earth elements.

In one aspect, the invention resides in a thin film electrical heating element including a thin film of tin oxide on an electrically insulating substrate, the film being doped with cerium and lanthanum and being substantially free of fluorine.
In another aspect, the invention resides in a method for the manufacture of a thin film heating element including the steps of depositing said film by pyrolysis of a solution of monobutyl tin trichloride containing cerium and lanthanum.

While some benefit will be obtained from quite low concentrations of the rare earth dopant, minimal effects will be observed with concentrations of 0.01 mol %, and preferred concentrations of each of the cerium and lanthanum are between approximately 1.25 mol % and approximately 3.75 mol %. Generally speaking the concentration of these rare earths will be chosen as that which contributes to film stability at the power densities for which the film is intended. Best results for films intended for operation at 20 Watts cm^{-2} have been obtained using equal concentrations of approximately 2.5 mol %.

The film is preferably doped with substantially equal quantities of donor and acceptor elements, the preferred dopants being antimony and zinc. The concentrations of both antimony and zinc will be influenced by the resistivity which is required. We have found concentrations in the region of 2.8 mol % to be suitable for heating element applications.

A useful characteristic of such films in their application as heating elements arises from the positive temperature coefficient resistance of the film. This enables elements to be produced which are self-regulating, in that they will initially operate at a higher wattage and, with increasing temperature, stabilise at the lower design wattage.

The substrate material will of course be chosen to suit the application. Suitable substrates include glass ceramic and non-oxide ceramic substrates as well as metallic substrates coated with high-temperature stable, electrically-insulating materials.

The preferred substrate temperatures for applying the base solution with dopants range from 500 to 750°C. Preferably, for application at 500°C, post annealing at approximately 600°C for at least one hour is carried out to help to stabilise the film.

Films according to this invention were manufactured from a solution using the spray pyrolysis process. For this purpose, monobutyl tin trichloride was used as a base solution, with 2.8 mol % antimony chloride, 2.8 mol % zinc chloride, 2.5 mol % cerium and 2.5 mol % lanthanum.

These films were fabricated with effective resistances of 26 ohm, 30 ohm and 45 ohm to enable heaters of 2.2 kW, 1.8 kW and 1.2 kW respectively to be used, powered by a 240V mains supply voltage. The films were selectively deposited using high temperature masking inks which were removed by brushing after deposition of the film. The films deposited had a high degree of transparency. The resistive properties of the heating elements remained unchanged after 2500 cycles (40 minutes on and 20 minutes off) at 650°C.

As indicated above, the positive temperature coefficient of resistance of these elements enables a self-regulating characteristic to be obtained, with an initially high power dissipation which may be of advantage in achieving more rapid rise to operating temperature. Fig. 1 shows the typical behaviour of the elements, where power dissipation is plotted against time of operation. As will be observed, the dissipation of the element commences at a high level and decreases as the resistance of the element increases with temperature, until a steady state condition is achieved at the design power consumption. Upon temporary cooling of the element, for example through contact with a cooler body to be heated, power dissipation will temporarily increase, assisting in achieving rapid heating.

Fig. 2 shows the relationship between temperature and power at steady state for five elements having power ratings between 500 and 1330 watts.

Life tests have shown that the films are particularly stable on inert substrates like quartz 96% silica in temperatures up to 650°C with power densities in excess of $15.5W/cm^2$. The films on lower grades of glass ceramics having impurities such as zinc were stable above 500°C at extremely high power densities.

Sheet resistances varying from around 60 ohms to above 400 ohms have been fabricated by varying the number of spray passes. The thin film thickness could be varied between 2000 Angstrom Units to around 14000 Angstrom Units by varying the number of spray passes. The films were deposited on various substrates including glass ceramics, alumina, silica glass and silicon nitride.

As well as their suitability in high temperature and/or high rise time applications, films made in accordance with the invention may be used in low temperature applications, such as comfort heating, refrigerating defrost, and general heating. Heating elements of tubular shape manufactured using the above technology can be used in heat exchangers for flow applications, air-conditioning re-heaters, hair dryers, washing and drying appliances, and can also be used as radiating surfaces.

DATED this 18th day of September 1998

EMAIL LIMITED
Patent Attorneys for the Applicant:
HALFORD & CO

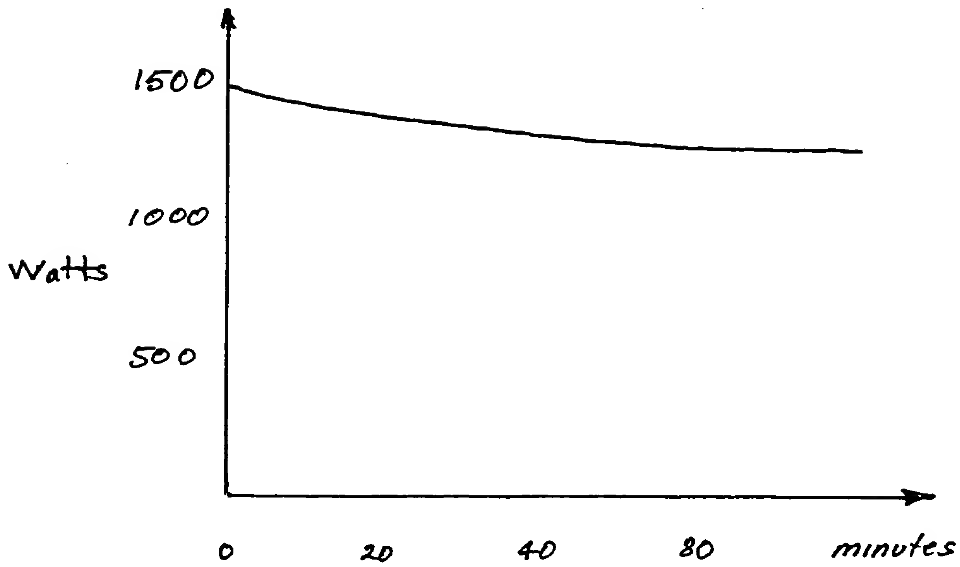
1500
1000
Watts
500
0
20
40
80
minutes

Fig. 1

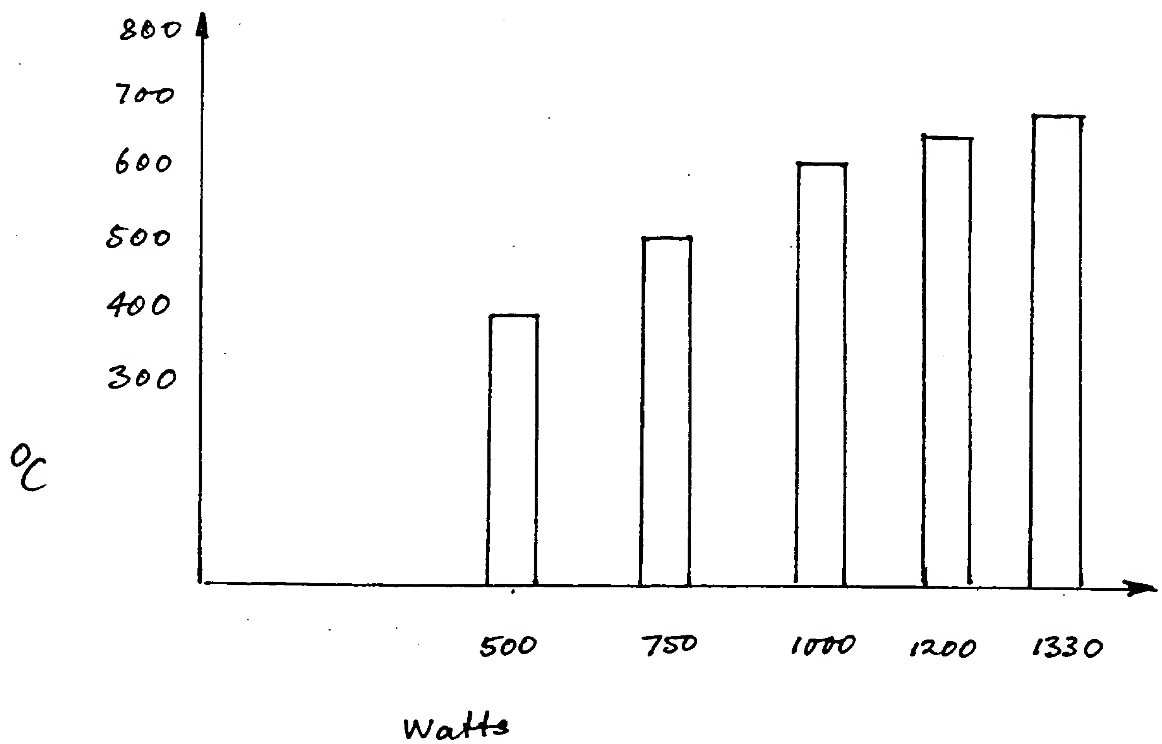
800
700
600
500
400
300
°C
500
750
1000
1200
1330
Watts

Fig. 2

SOLID ALUM SALT-BASED PRODUCTS IN A LIQUID DISPENSING CONTAINER

Description

Just add water product technology: A crystal of mineral salts is grown in a pump mist spray bottle.

The crystal forms as a solid in the bottom of the bottle. when water is added this will dissolve a small amount of the minerals into the water creating a product that can be used for treatment of mouth ulcers (canker sores) , cold sores , skin rashes like dermatitis, psoriasis, tinea, as a blood stop, for suture wound and umbilical care. in first aid applications for cuts burns or abrasions. Marine stings , insect bites, Sun burn. Antiseptic wound sealer. It may also be used as an anti Bacterial deodorant. when the bottle is empty of spray you simply re fill it with water and it makes more product instantly. We can make products that refill 5, 10 , or twenty times so its like 20 bottles of product in one. This also creates an new system of environmental grade 1 products , because it reduces the amount of waste plastic bottles entering the environment as land fill. Its twenty times less use of power resources to produce the product and twenty times less consumption and greenhouse effect upon the environment.

Background History and Art.

Alum is an inorganic compound and generally contains two metals two sulfate groups and water. A compound of this type is called a hydrated Double salt. Alum's included hydrated double salts. That have similar compositions and similar crystalline structures. The description of alum also includes Aluminum Sulfate, Aluminum Chlorohydrate and Aluminum chlorydroxide.

Alum's have a variety of uses. For instance Alum's have been used in the dying industry, for water purification, for paper sizing, for fire proofing fabrics, in fire extinguishers, and in medicinal and cosmetics fields.

It is the medicinal and cosmetics fields where alum's have particular interest. For instance alum has astringent properties, and is used in medicine to treat certain skin conditions, and to stop bleeding from small cuts. dilute solutions (1-4%) have been used as mouth washes and gargles. solutions of 5-10 % are used to harden the skin. especially of the feet Strong aqueous solutions of alum are used as styptic for minor cuts and abrasions. Recent applications of alum containing solutions include bladder irrigation's for hemorrhaging Alum is an important chemical compound with great benefits across a broad spectrum of issues to mankind.

commercially alum's include Aluminum Sulfate, potassium alum and ammonium alum and include all alum based salt

Sulfate groups known to science as alum based sulfates. Ammonium alum is manufactured by Crystallization from an aqueous solution of ammonium sulfate and aluminum sulfate. Ammonium alum crystals are also produced by treating a mixture of aluminum sulfate and sulfuric acid with ammonia. Potassium alum occurs naturally in the minerals alunite and kalinite.

It is known that alum's , Alum sulfate and especially potassium and ammonium alum can be used as a deodorant for human use in liquid form. The alum salts are highly dissolvable in water. To make an effective solution , 5-10 % by volume weight of alum may be added. If to much of the alum salts are added to a liquid medium it results in an over saturation of suspended salts which presents the following problems. pump spray bottles become blocked and clogged with salt crystals in the spray head and the pump spray tube.

Prior Art

It is known that alum salts may be plasticized with additives such as Art work disclosed in Patent no 693744 in Australia entitled A moldable Alum Composition (The Invention Of this Author)□

This Patent relates to forming Alum solids that are demolded for use. Not to alum solids that are dissolved by water the subject of this Technology.

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Technical object

It is the object of this invention to create an Alum based end product that can be refilled with water to dissolve in precise saturation doses so that it does not block up the spray pump head and to form a product that can be conveniently refilled by consumers with water to make more product instantly.

To over come the suspension saturation problem it has been discovered that the solid alum salts solution strength and rate may be controlled by direct volumetric exposure to a liquid in a dispensing container. The diagram marked as figure 1 is used to highlight the method . in the diagram the bottle has a solid of alum crystal in the bottom. The side walls and bottom of the alum are sealed tight against the walls and are not exposed to the water, only the top surface area of the alum is dissolved. The water reaches saturation point and can not dissolve any more alum. Figure 2 is a capitale devise that may be filled with Alum and the dropped into the bottle for dispersion of Alum and additives.

METHOD 1

Heat 500 grams of granulated Alum at 100 c add 10 grams of glycerin . When the alum has melted into a liquid or is substantially liquid it is then poured into a pre determined liquid dispensing container. (Packaging) The hot liquid alum solidifies upon cooling forming a three dimensional shape with one face exposed to form a saturated solution when water is added. The side walls and bottom of the Alum compound is sealed to the water being added so that over ionization and solution saturation cannot occur as disclosed in the Non commercial example.

METHOD 2

Heat 500 grams of Alum in a 1000 watt micro wave on high for 15 minutes. Add 25 grams of glycerin . When finished cooking bring out of the micro wave and re hydrate by adding water back to 480 grams. Allow to cool to 50 degrees C and place into bottle or captule container where the Alum mixture will recrystalise into a solid.

METHOD 3

Follow method 1 but do not add any additives , allow to cool but still liquid and pour into containment devise.

The above Methods detail various formula's with or without additives, if additives are desired they may be added from .05 percent to 50 % by weight of alum.

it can be seen by using the above described methods that a refillable with water product is made for use in the cosmetics , medicinal and veterinary industries.

Non Commercial Examples

If Alum compounds or granules of alum compounds are placed into a liquid pump spray, when water is added this will result in an over saturation of the dissolved salts and block and clog up the spray head as per figure 3

The combined surface area of the alum granules interacting with the liquid results in super saturated solution that will block and clog the spray pump head and tube. It seems (without wishing to be bound by theory)That an over ionization process occurs of the base water acting upon the positive electrons on the acidity of the Alum Salts. This leads to small crystals and granules of the alum dropping out of the solution and settling in the container which are sucked up the spray head tube and blocking it. even if filters etc. are placed on the spray tube preventing these granules entering the tube the solution is far to strong and causes the spray top to become blocked and clogged.

COMPOUNDS CLAIMED : The Alum Group Of Compounds

The Group Of Alum's claimed are any of the water soluble alum's which may be melted by heat and solidified in liquid dispensing devises. Aluminum Sulfate, ammonium alum , potassium alum or any alum based compounds that create the same effect and end use products of water solubility and refill technology the subject of this invention.

Claimed Additives

Glycol's and organic polyols such as glycerin or fragrances may be added, from .o5 to 50 % of additive may be used. other Medicinal compounds may be used .

CLAIMS

1)A method whereby Alum Based Compounds including additives (additives Do not necessarily have to be used) are used to form water soluble solids in a liquid Dispensing Devise, Water based liquid carriers are Claimed so that precise doses of the alum salts may interface with a liquid Carrier is central to this invention.

2) An environmental grade 1 technology because products formed last longer than others and this prevents a large quantity of waste in packaging going into land fill and reduces green house gas effects.

3) Alum products do not have to be demoulded for use.

4) a method of heating the Alum into liquid and pouring or injecting , pumping or placing it into a liquid dispensing devise so that only one surface area of Alum is capable of being dissolved when water is added.

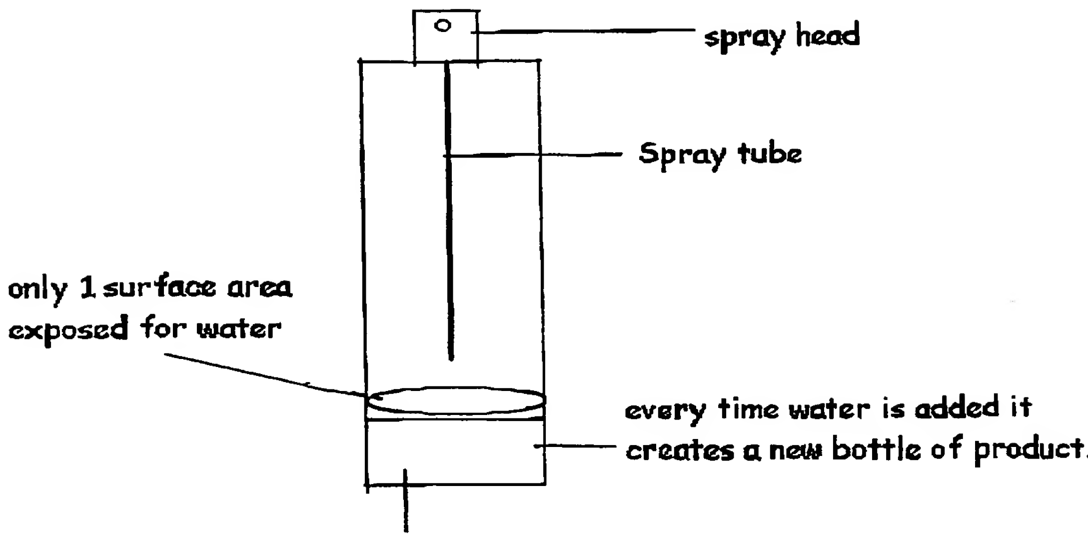
5) A method of Creating a captule devise filled with alum that can be placed directly into a liquid dispensing devise so that precise doses of alum may interface with water when added .

6) All Alum Based water soluble compounds are claimed.

7) Additives such as organic polyols and fragrances can be used in creating a solid Alum compound for dispersal by dissolution in water ready for end use.

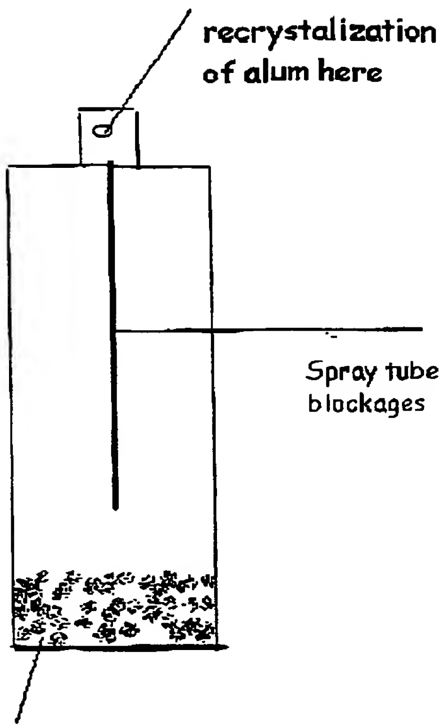
8) Spray pump ,roll on or other liquid dispensing devises containing alum based compounds that are refillable with water for use, as described in the embodiment of this artwork.

FIG 1



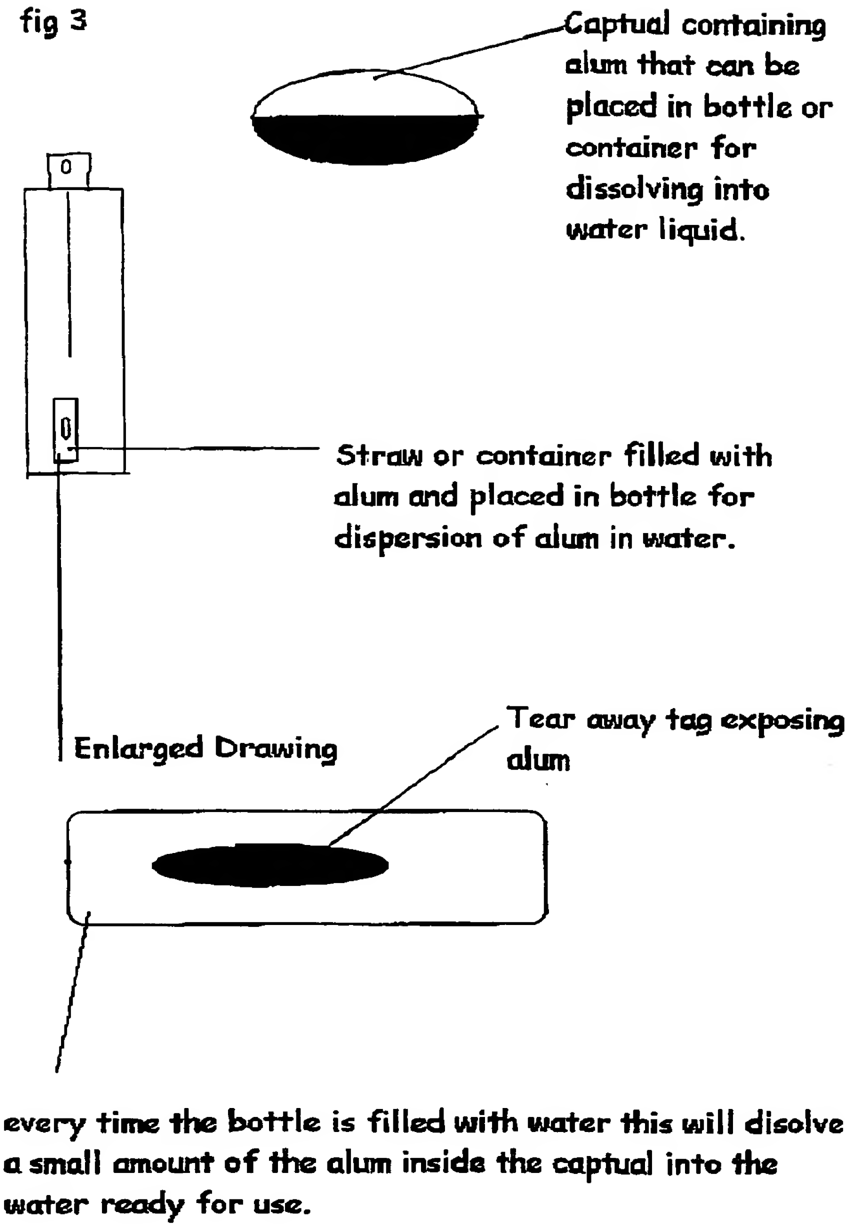
Alum Liquid solidifys to creat solid , the side walls
and bottom of the alum form a water tight-seal
preventing over ionization and saturation.

fig2



Alum grannuals in bottom of container This is where over ionization occurs dissolving to much alum into the water leading to spray head blockage.

fig 3


Captual containing alum that can be placed in bottle or container for dissolving into water liquid.
Straw or container filled with alum and placed in bottle for dispersion of alum in water.
Enlarged Drawing
Tear away tag exposing alum
every time the bottle is filled with water this will disolve a small amount of the alum inside the captual into the water ready for use.